

# PATENT SPECIFICATION

(11)

1 270 077

NO DRAWINGS

1 270 077

- (21) Application No. 54087/70 (22) Filed 13 Nov. 1970  
(31) Convention Application No. P 19 64 998.0 (32) Filed 24 Dec. 1969 in  
(33) Germany (DT)  
(45) Complete Specification published 12 April 1972  
(51) International Classification C08G 22/10 17/13  
(52) Index at acceptance  
C3R 32D1 32E2 32E3 32E4 32E9 32G2 32J1 32J2Y 32J3  
3D20 3D2A 3D4 3N7  
(72) Inventors KLAUS KÖNIG  
ERWIN MÜLLER  
CORNELIUS MÜHLHAUSEN  
UWE JENS DÖBEREINER



## (54) PROCESS FOR THE PRODUCTION OF POLYURETHANE ELASTOMERS

(71) We, FARBENFABRIKEN BAYER AKTIENGESellschaft, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The production of polyurethane elastomers from high molecular weight hydroxy compounds, diisocyanates and chain lengthening agents has frequently been described in the literature. Elastomers which are resistant to hydrolysis can be obtained, for example, as described in German Patent Specification No. 1,218,717 if the high molecular weight hydroxy compound which is used is a polyester of hexane-1,6-diol and adipic acid. A further improvement in the resistance to hydrolysis can be achieved by the process described in French Patent Specification No. 1,540,799 by using, as the high molecular weight hydroxy compound, a hexane-1,6-diol polycarbonate which is obtained by ester interchange of hexane-1,6-diol, for example, with diphenyl carbonate.

20 Both the polyester of hexane-1,6-diol and adipic acid and the hexane-1,6-diol polycarbonate have a waxy consistency and soften only above 45°C. The softening point of the high molecular weight hydroxy compound largely determines the freezing point of the elastomers which are obtained from this compound (the freezing point drops with decreasing softening point and conversely). Hence, the elastomers obtained from these high molecular weight hydroxy compounds are resistant to hydrolysis but have a freezing temperature of about -21°C. On further cooling, these elastomers lose their elasticity and are converted into a glassy state (glass transition temperature).

45 Because of this behaviour, elastomers of

this type have only a limited use at low temperatures. Even when using mixtures of the two above mentioned high molecular weight hydroxy compounds, the freezing temperature or glass transition temperature of the elastomers which are obtained from them is only insignificantly altered.

The present invention is based on the finding that polyurethane elastomers which have a low freezing point and a high resistance to hydrolysis can also be obtained if the high molecular weight hydroxy compounds which are reacted with diisocyanates and chain lengthening agents are those which are obtained by condensation of hexane-1,6-diol, adipic acid and a diaryl carbonate, preferably diphenyl carbonate.

The present invention relates to a process for the production of polyurethane elastomers by reacting high molecular weight hydroxy compounds which have a molecular weight of 800 to 2500, diisocyanates and low molecular weight compounds which have a molecular weight of up to 400 and which contain at least two hydrogen atoms that are reactive with isocyanates, which process is characterised in that the high molecular weight hydroxy compounds used are condensation products of hexane-1,6-diol, adipic acid and diaryl carbonate.

The surprising observation was made that the elastomers produced from the high molecular weight hydroxy compounds according to the invention have both a very low freezing point and a very good resistance to hydrolysis in addition to excellent mechanical properties.

The freezing point and resistance to hydrolysis of the elastomers depend on the proportions in which the three components which yield the high molecular weight hydroxy compound according to the invention are used. Thus, when high molecular weight hydroxy compounds are prepared from hexane-1,6-diol and adipic acid with the

addition of only a small amount of diphenyl carbonate, the properties of the elastomers obtained are similar to those obtained from polyesters of hexane-1,6-diol and adipic acid.

Conversely, when using only minor quantities of adipic acid, the elastomers obtained resemble the products described in French Patent Specification No. 1,540,799.

The most satisfactory proportions for the process of the present invention are when hexane-1,6-diol and adipic acid are used in a molar ratio of 10:1 to 3:2 and the quantity of diaryl carbonate is calculated so that the molecular weight of the resulting high molecular weight hydroxy compound is approximately 2000. The high molecular weight hydroxy compounds obtained from components used in these proportions are pasty in consistency and have a softening point below 30°C. They are particularly suitable for the production of elastomers which have a high resistance to hydrolysis and low freezing point; the resistance to hydrolysis of the resulting elastomers is surprisingly only insignificantly altered by the adipic acid which has been incorporated into the molecule.

The preparation of the high molecular weight hydroxy compounds which are used according to the invention is carried out by known methods. If desired, the three components may be condensed in the preferred proportions in one step, phenol and water being split off at the same time, until the required hydroxyl number is reached. It is advisable, however, to carry out the condensation of adipic acid with hexane-1,6-diol, which proceeds with elimination of water, in a first stage until an acid number of approximately 1 is reached, preferably using hexane-1,6-diol and adipic acid in the molar ratio of 6:1, and then in a second step to carry out the reaction with the diaryl carbonate, preferably diphenyl carbonate. Unwanted side reactions consisting in premature saponification of the diaryl carbonate or esterification of adipic acid with the phenol which has been split off are thus prevented.

The reaction of the high molecular weight hydroxy compounds according to the invention with diisocyanates and chain lengthening agents is carried out by methods which are known *per se*. It may be carried out in the melt or in solvents according to several methods. Thus, for example, the high molecular weight hydroxy compound may be reacted first with an excess of a diisocyanate to produce a prepolymer which, after the addition of a chain lengthening agent (a low molecular weight compound containing at least two hydrogen atoms which are reactive with isocyanates), is shaped by casting or, if desired, is converted after it has been hardened into a granulate which can then be moulded under pressure at elevated tem-

peratures.

According to another procedure, the chain lengthening agent is added to the high molecular weight anhydrous hydroxy compound which is used according to the invention, and the mixture of the two hydroxy compounds is then reacted with an excess or an equivalent or less than equivalent quantity of diisocyanate. If the diisocyanate is used in equivalent or less than equivalent quantity, the products obtained are stable on storage and can be rolled, and, after other diisocyanates have been rolled into them (in particular dimeric toluylene diisocyanate), they can be cross-linked in a moulding process at elevated temperature.

If the chain lengthening agents used are compounds which, in addition to the two hydrogen atoms which are reactive with isocyanates, also contain reactive groups such as glycerol monoallyl ether or di- $\beta$ -hydroxyethyl-m-toluidine, the cross-linking which takes place during moulding may also be effected with sulphur, formaldehyde or peroxides.

Suitable diisocyanates for use in the present invention include the known aliphatic, cycloaliphatic, araliphatic and aromatic diisocyanates, in particular 1,5-naphthylene-diisocyanate, 4,4'-diphenylmethane diisocyanate, p-phenylene diisocyanate, toluylene diisocyanates, xylylene diisocyanates, hexamethylene diisocyanate and isophorone diisocyanate.

Suitable chain lengthening agents include the conventional chain lengthening agents having a molecular weight of up to 400, i.e. compounds which contain at least two hydrogen atoms which are reactive with isocyanates. Particular examples include the various types of glycols such as butane-1,4-diol, butane-2,3-diol, butene-1,4-diol, ethylene glycol, neopentyl glycol, p-phenylenedi- $\beta$ -hydroxyethyl ether, as well as diamines such as 3,3'-dichloro-4,4'-diamino-diphenylmethane and the various diamines which contain ester groups, e.g. 3,5-diamino-4-chlorobenzoic acid esters, as described in British Patent No. 1,220,310. Higher functional chain lengthening agents, e.g. triols such as trimethylol propane or glycerol or diethanolamine may be used in proportions of up to 50% based on the weight of the difunctional chain lengthening agents used.

Suitable diaryl carbonates include diphenyl carbonate, ditolyl carbonate, dinaphthyl carbonate and di-p-chlorophenyl carbonate; diphenyl carbonate is preferred.

The products of the process may be used for many different purposes, e.g. as sealing compounds, machine parts, plastics articles and shoe sole material. The products of the process may generally be used in all those fields in which polyurethane elastomers are used.

*Examples:**Starting materials:**A<sub>1</sub>:*

3068 g (26 mols) of hexane-1,6-diol were esterified with 1898 g (13 mols) of adipic acid in a melt in a 10 litre three-necked flask equipped with a stirrer, contact thermometer and a packed distillation column, the temperature being raised from 130°C to 200°C in the course of 5 hours while the water of condensation was distilled off. A moderate stream of CO<sub>2</sub> was then passed through the melt at 200°C for 8 hours to complete esterification. The last residues of water were removed at 130°C and 12 mm Hg. A waxy mixture of diols of OH number 318 (calculated 324) and acid number 1.5 was obtained.

2354 g (11 mols) of diphenyl carbonate were then introduced into the reaction vessel and the mixture was heated with stirring at 12 mm Hg. Phenol began to distil off between 130 and 145°C. The temperature was raised to 200°C in the course of 12 hours according to the rate of distillation. At the end of that time, 2020 g (97.5% of theoretical) of phenol had distilled off. The pressure was then reduced to 0.5 mm Hg and stirring was continued for 6 hours at 200°C. A further 40 g of phenol were obtained. Total quantity: 2060 g (99.75% of theoretical).

A yellow viscous oil of OH number 43.6 (calculated 46.1) was obtained.

*A<sub>2</sub>:*

7080 g (60 mols) of hexane-1,6-diol and 2190 g (15 mols) of adipic acid were esterified to give a diol mixture of OH number 567 (calculated 577) in a manner analogous to *A<sub>1</sub>*. Ester interchange with 8350 g (39 mols) of diphenyl carbonate yielded a low melting wax of OH number 51.0.

*A<sub>3</sub>:*

4248 g (36 mols) of hexane-1,6-diol were esterified with 875 g (6 mols) of adipic acid to yield a diol mixture of OH number 680 (calculated 685).

The reaction of 4610 g (28 mols) of the diol mixture with 5243 g (24.5 mols) of diphenyl carbonate in a manner analogous to *A<sub>1</sub>* yielded a soft wax of OH number 72.8 (calculated 74.5).

*Example 1*

2560 g (1 mol) of the polyester polycarbonate *A<sub>1</sub>* and 658 g (3.14 mols) of 1,5-naphthylene diisocyanate are stirred together at 126°C. After 10 minutes under vacuum, 180 g (2 mols) of 1,4-butane diol are introduced into the melt. After thorough mixing, the mixture is poured into wax-lined moulds and then heated for 24 hours at 100°C. The moulded products have the properties given under 1 in the table.

*Example 2*

In a manner analogous to Example 1, 2200 g (1 mol) of polyester polycarbonate *A<sub>2</sub>* are reacted with 552 g (2.63 mols) of 1,5-naphthylene diisocyanate and 110 g of (1.22 mols) 1,4-butane diol. The properties of the moulded products obtained are given under 2 in the table.

*Example 3*

In a manner analogous to Example 1, 1540 g (1 mol) of polyester polycarbonate *A<sub>3</sub>* are reacted with 407 g (1.94 mols) of 1,5-naphthylene diisocyanate and 61.6 g (0.685 mol) of 1,4-butane diol. The moulded products obtained have the properties given under 3 in the table.

*Comparison Examples:**Example I*

The reaction of 2000 g (1 mol) of a hexamethylene polycarbonate of OH number 56 with 357 g (1.7 mols) of 1,5-naphthylene diisocyanate and 40.5 g (0.45 mol) of 1,4-butane diol in a manner analogous to Example 1 results in moulded products which have the properties given under I in the table.

*Example II*

An elastomer prepared in a manner analogous to Example 1 from 2000 g (1 mol) of a polyester of adipic acid and hexanediol of OH number 56, 357 g (1.7 mols) of 1,5-naphthylene diisocyanate and 40.5 g (0.45 mol) of 1,4-butane diol has the properties given under II in the table.

Examples and Comparison Examples	Table						Glass transition temperature °C.					
	Shore hardness A	Shore hardness D	Tensile strength kg/cm <sup>2</sup>	Elongation at break %	Recoil elasticity kg/cm	Dimensional stability						
Ageing by storage in water at 100°C —Tensile strength after days in kg/cm <sup>2</sup>												
	2	4	7	14	28							
1	95	45	456	512	54	60	369	281	189	64	destroyed	—46°
2	94	45	496	419	50	66	398	306	223	110	"	—44°
3	95	45	584	361	43	45	430	385	263	131	101	—41°
I	90	—	282	423	48	40	252	248	230	170	130	—22°
II	89	—	305	445	49	43	235	155	118	destroyed		—21°

## WHAT WE CLAIM IS:—

1. A process for the production of a polyurethane elastomer which comprises reacting together at least one of each of:

- (a) a diisocyanate,
- (b) a chain lengthening agent which contains at least two hydrogen atoms which are reactive with isocyanates, and has a molecular weight of up to 400, and
- (c) a high molecular weight hydroxy compound which has a molecular weight of 800 to 2500 and is a condensation product of 1,6-hexanediol, adipic acid and a diaryl carbonate.

2. A process as claimed in claim 1 in which the compound (c) is prepared using a hexane-1,6-diol to adipic acid molar ratio of 10:1 to 3:2 and the amount of diaryl carbonate used is such that the compound (c) has a molecular weight of approximately 2000.

3. A process as claimed in claim 1 or claim 2 in which compound (c) is prepared by a single stage condensation of the three components.

4. A process as claimed in claim 1 or claim 2 in which in the preparation of compound (c), the hexane-1,6-diol and the adipic acid are reacted together in a first stage and this product is then reacted with the diaryl carbonate.

5. A process as claimed in claim 4 in which the molar ratio of hexane-1,6-diol to adipic acid is 6:1.

6. A process as claimed in any of claims 1 to 5 in which the diaryl carbonate used is diphenyl carbonate.

7. A process as claimed in claim 1 substantially as herein described with reference 50 to any one of the Examples.

8. Polyurethanes when produced by a process as claimed in any of claims 1 to 7.

ELKINGTON AND FIFE,  
Chartered Patent Agents,

High Holborn House,  
52/54 High Holborn,  
London W.C.1.

Agents for the Applicants.